

Water in Different Poly(styrene sulfonic acid)-Grafted Fluoropolymers

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ABSTRACT: We investigated the water present in a series of radiation-grafted fluoropolymers with similar poly(styrene sulfonic acid) (PSSA) contents with the aim of determining the influence of the initial fluoropolymer. Radiation-grafted membranes were compared with Nafion 117 and 105. Sorption curves and differential scanning calorimetry thermograms showed that all the membranes contained the same number of water molecules tightly bound to the sulfonic acid groups; this water did not freeze. In radiation-grafted membranes, the content of freezing water absorbed from the liquid-phase water varied according to the swelling abilities of the membrane, which were dependent on the initial fluoropolymer. Larger pores accompanied high water

uptakes and high conductivity. The amount of water absorbed from the vapor phase was similar for all radiation-grafted membranes with similar PSSA contents, irrespective of matrix material. Nafion membranes had higher conductivities at intermediate hydration levels, and the relaxation times measured by NMR were longer than for the radiation-grafted materials. This suggests that the channels for water and proton conduction are different in the two types of materials. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 33–42, 2002

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INTRODUCTION

Radiation grafting is an interesting route for the preparation of ion-exchange membranes because of the degree of control it offers over the synthesis and the low costs involved. A common approach is to irradiate a commercially available preformed fluoropolymer film with an electron beam and then place it in a styrene solution. The polystyrene grafts formed are subsequently sulfonated. The initial film acts as a host for the proton conducting poly(styrene sulfonic acid) (PSSA) grafts. Such membranes are promising materials for solid polymer electrolytes in low-temperature fuel cells.^{1,2} Many initial fluoropolymer films have been investigated,^{1–4} but researchers have generally focused on one type of initial fluoropolymer and have then studied the properties of the membrane as a function of the amount of PSSA added to the film. As each group favors slightly different preparation conditions, comparisons of properties and performance are impossible. Hence, the exact influence of the na-

ture of the initial fluoropolymer film is unclear. In a previous study, we investigated the preparation and structure of a series of different fluoropolymer-based materials with similar PSSA contents;⁵ here, we investigated the influence of the fluoropolymer on the water present in the membranes.

Water management properties are an important aspect of any membrane to be used in fuel cells: the water content influences the proton conductivity of polymer electrolyte membranes,⁶ the volume change, mechanical properties, and factors such as the gas permeability.⁷ Investigating the role of water in different types of membranes, therefore, not only offers an insight into variations in morphology but is also of practical importance.

In this work, our aim was to determine the influence the fluoropolymer moiety has on the water in the membranes and, more generally, to compare the radiation-grafted membranes with commonly used Nafion* materials.

EXPERIMENTAL

The starting materials were commercially available fluoropolymer films obtained from various sources: 80 μm poly(vinylidene fluoride) (PVDF) was purchased

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TABLE I
Membrane Properties

| Matrix | Degree of grafting (%) | Thickness wet (μm) | Matrix DSC crystallinity ⁵ (%) | Water uptake from liquid (g/g) | IEC (meq/g) | λ at 100% RH (after immersion in water) | Conductivity (mS/cm) at 100% RH (after immersion in water) |
|-----------------|------------------------|---------------------------------|---|--------------------------------|-------------|---|--|
| PVDF a | 39 | 130 | 40 | 0.79 | 1.83 | 23 | 66 |
| PVDF b | 39 | 70 | 41 | 0.67 | 1.83 | 20 | 72 |
| ETFE | 31 | 90 | 15 | 0.82 | 1.51 | 32 | 43 |
| PVDF-co-HFP 6% | 39 | 130 | 27 | 0.99 | 1.81 | 30 | 63 |
| PVDF-co-HFP 15% | 40 | 120 | 20 | 1.51 | 1.94 | 39 | 110 |
| FEP | 34 | 145 | 15 | 1.00 | 1.80 | 30 | 108 |
| Nafion 117 | — | 210 | — | 0.35 | 0.89 | 21 | 51 |
| Nafion 105 | — | 150 | — | 0.50 | 1.00 | 24 | 56 |

from Goodfellow, 40 μm PVDF was obtained from Structur Oy (Solef 1010), 50 μm poly(ethylene-alt-tetrafluoroethylene) (ETFE) was obtained from Nowoflol (Nowoflon ET), and 80 μm poly(vinylidene-co-hexafluoropropylene) (PVDF-co-HFP) [Kynarflex[®] 2750 and 2850, containing 15 and 6% hexafluoropropylene (HFP), respectively] was obtained from Elf Atochem.

Details of the grafting and sulfonation can be found elsewhere.⁵ The dry weight of all samples was determined after drying the samples at room temperature in a desiccator over P_2O_5 to a constant mass. We pretreated Nafion 105 and 117 samples by boiling them for 30 min in a 5% H_2O_2 solution, rinsing three times in hot water for 1 h, boiling for 1 h in 0.5M H_2SO_4 , and rinsing three times in hot water for 1 h. We pretreated radiation-grafted samples by boiling them in 0.5M H_2SO_4 and then rinsing them in hot water.

To measure the water uptake from the liquid phase, we boiled the samples in water for at least 1 h and then left them to equilibrate at room temperature. We removed excess water by blotting the surface. Samples were weighed immediately, and the ratio of the mass of water absorbed to the mass of the dry sample was calculated. We followed the sorption and desorption of water by the membranes by placing samples in a closed vessel containing a saturated salt solution and a small fan and leaving them to equilibrate for at least 5 days (preliminary tests showed that this was sufficient for equilibrium to be reached). The samples were then weighed and placed over the next solution. The salt solutions used and the corresponding relative humidities calculated were taken from Wexler.⁸

We determined the ion-exchange capacity (IEC) by immersing samples in a known volume of NaOH and titrating the excess NaOH against HCl, using Cresol Red as an indicator the following day.

Conductivities at different relative humidities were recorded by impedance spectroscopy. Measurements were carried out in a two-electrode cell with 0.071-cm² platinum electrodes connected to an Autolab PGSTAT 20 (Eco Chemie B.V.) instrument supplied with FRA

2.4 software. Before the measurements membranes were allowed to equilibrate over a salt solution and during the measurements, a salt solution was retained in the bottom of the cell. We determined membrane resistance by extrapolating the linear part and/or the semicircle to the real axis using data from a frequency range of 5–85 kHz. The conductivity was calculated from the resistance with the electrode area and membrane thickness; the latter was measured with a micrometer.

Differential scanning calorimetry (DSC) measurements were performed with a PerkinElmer DSC-7 instrument in the temperature range -50 to 10°C with a heating rate of $5^\circ\text{C}/\text{min}$. The calorimeter was calibrated with indium and water.

NMR experiments were carried out with a Varian UNITY INOVA spectrometer operating at 300 MHz for protons, equipped with a pulsed field gradient (PFG) probe. The temperature was set at 22°C . The longitudinal proton relaxation times were measured by the inversion recovery method with 25 suitably spaced delay times from 0.001 to 3 s. For the PFG NMR measurements, a stimulated echo sequence with a delay time of $\Delta = 11$ ms between the first and last 90° pulse was applied. Fifteen spectra were recorded over linearly incremented gradient strengths of 0–65 G/cm. The water self-diffusion coefficient ($D_{\text{H}_2\text{O}}$) was calculated from the slope of the signal intensity versus gradient strength, obtained with a regression fit of the raw data. We calibrated the instrument by measuring $D_{\text{H}_2\text{O}}$ of a water sample under the same experimental conditions.

RESULTS AND DISCUSSION

Details of the samples under consideration are given in Table I, which also gives the data obtained for Nafion 117 and 105. Although much data for Nafion samples have been published, the spread of data resulting from different procedures makes it imperative to record data for Nafion samples in parallel with the radiation-grafted samples if the results are to be compared.

Here, both the Nafion and the radiation-grafted membranes had sulfonate fixed ionic groups and were in the proton form. However, the IECs of the radiation-grafted materials were about double those of the Nafion samples, and the structures of the Nafion and radiation-grafted materials were different. The Nafion materials have been described as having a three-region structure: aqueous domains, hydrophobic domains, and an interfacial region of intermediate hydrophilicity.⁶ Many models have been proposed for the morphology of these materials,⁹ among others, a cluster¹⁰ and a tortuous cylindrical pore network.⁶

The fluoropolymers used as starting materials for the radiation-grafted materials are semicrystalline. Grafting takes place mainly in the amorphous regions and leads to phase separation.¹¹ Small angle x-ray scattering data collected after sulfonation suggest that there was some ionic aggregation in PVDF-*g*-PSSA. The Bragg distance between clusters was around 17–25 Å,^{12,13} which is less than the 30–50 Å reported for Nafion.^{10,14}

Sorption curves

Figure 1(a) shows the sorption data for the radiation-grafted and Nafion materials in terms of grams of water per gram of dry membrane. Figure 1(b) shows the data in terms of the number of water molecules per sulfonic acid group (λ). It can be seen that Nafion materials absorbed less water in absolute terms but that the gap between the membrane types was largely accounted for by the difference in IECs. It is also clear that the differences between the radiation-grafted materials were much reduced when the variations in IEC were taken into account. The data are qualitatively similar to that published by others for Nafion (see, e.g., refs. 15 and 16): at first the water content increased slowly with relative humidity (RH) and then, in a second region, the increase was much greater.

The water uptake pattern was consistent with successive steps in the hydration of the membrane described by Pletcher:⁶ in the dry state, the counterions are tightly bound to the sulfonate groups. Water first solvates the fixed ionic groups and counterions. When more water is absorbed, the polymer swells, and the hydrophilic zones start to resemble an aqueous electrolyte. The data shows that the primary hydration of the sulfonic acid groups continued up to around 90% RH and was roughly identical for all the samples, which suggests it was largely independent of structure. The water uptake at this stage reached about nine molecules of water per sulfonic acid group. The membranes differed mainly in how much water they took up thereafter. The enthalpy of water sorption in these two steps has been shown to be different:^{6,17} the enthalpy of the first step is greater than that of water liquefaction; that of the second step smaller. The second part of the sorption

is assigned to the absorption of water into pores and leads to the swelling of the membrane. The rearrangement of the polymer during expansion results in an endothermic contribution. The increase in entropy then drives the absorption of water.

The desorption of water was also studied. Samples were first immersed in boiling liquid water for 1 h and then left to equilibrate in water at room temperature. Afterward, the surface was blotted dry, and the sample was placed immediately at 100% RH. After several weeks and contrary to the observation of Zawodzinski et al.,¹⁸ the water content of the samples did not decrease to the content determined at 100% RH after water sorption from the vapor phase alone. In Nafion 117, for samples placed successively in atmospheres of increasing RH, λ reached 14 at 100% RH, whereas in samples first immersed in liquid-phase water, $\lambda = 21$. For all membranes, λ decreased by only two to three molecules per sulfonic acid group when the samples were transferred from liquid water to 100% RH, a difference that could be due to a loss of excess water from the surface of the samples. The gap in the water contents on sorption and desorption existed only in the 90–100% RH range and appeared, therefore, to reflect differences in the rearrangement process.

This difference in the sorption and desorption behavior was particularly striking in the radiation-grafted materials: the water uptake from liquid-phase water of radiation-grafted membranes has already been shown to vary with the crystallinity of the material.⁵ Figure 2 confirms this but also shows that the crystallinity appeared to play no part in determining the water uptake from the vapor phase. The difference between the water uptake of Nafion 117 from liquid and vapor phases has been attributed by Zawodzinski et al.¹⁸ to differences in the sorption processes in liquid water and water vapor. They suggest that all the pores are filled by the liquid, whereas water uptake from the vapor phase relies on capillary condensation, which is hindered by the hydrophobic surface of the Nafion materials. The difference in the water uptake of the radiation-grafted materials from the liquid and vapor phases, with an influence of the crystallinity in one case and no influence in the other, suggests that the process is indeed different. A possible explanation is that when the radiation-grafted membranes were placed in boiling water, the water uptake was accompanied by a significant rearrangement and swelling of the polymer. The fluoropolymer matrix then played a part in restricting the expansion, and the ultimate swelling depended on the matrix crystallinity. When water was desorbed, the PSSA grafts rearranged, and some part of this rearrangement appeared to be irreversible at room temperature. If thereafter the RH was increased, the membranes expanded again but to a lesser extent. The reorganization was then limited by

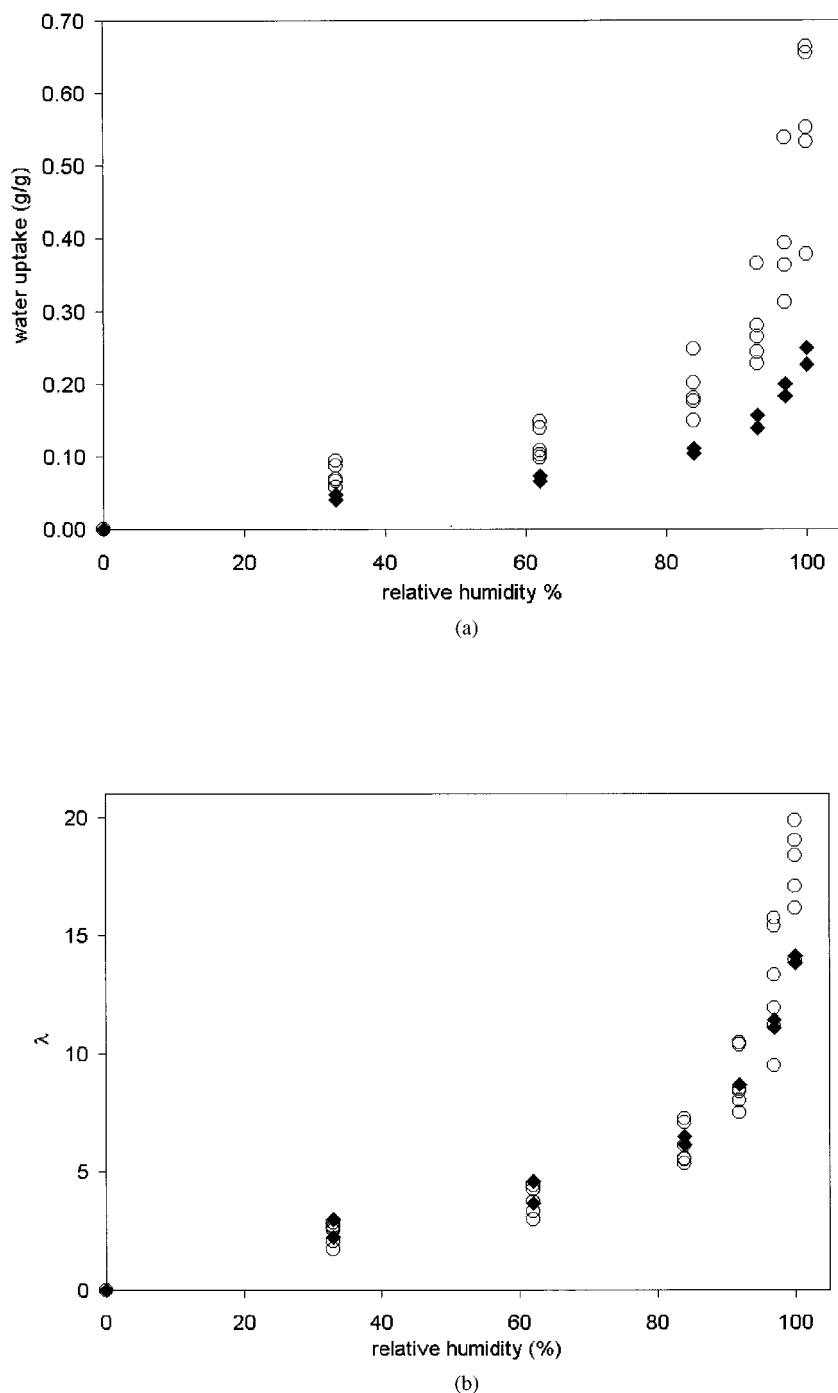


Figure 1 Water sorption versus RH in terms of (a) g/g and (b) λ for (○) radiation-grafted and (◆) Nafion membranes.

the arrangement of the PSSA grafts adopted in the dry state. The membranes swelled less than during the water uptake in boiling water, and all the fluoropolymer matrices could accommodate the expansion without rearrangement.

This result is of practical importance for membranes to be used in fuel cells because it shows that the water uptake properties of the membrane will differ according to the procedures used in the membrane electrode

assembly and, once in the fuel cell, before and after any drying out that may occur on the anode side. The rehydration process may be incomplete if humidification from water vapor is used.

When the RH reached 97%, RH drops appeared on the surface of the radiation-grafted materials but not on the surface of the Nafion materials, pointing to a lesser surface hydrophilicity of the latter. This could be partly accounted for by the lower IECs of these materials.

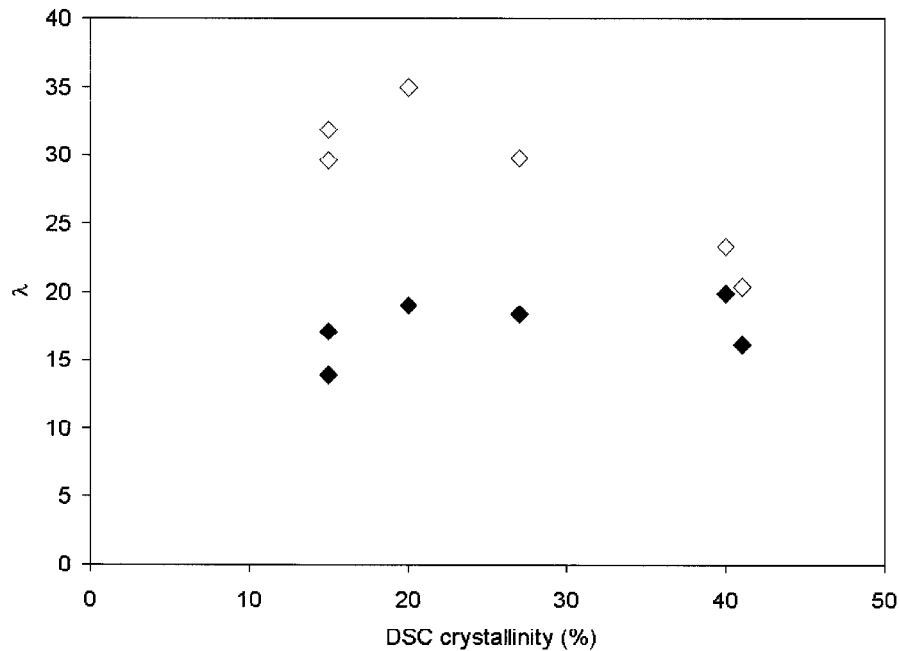


Figure 2 λ at 100% RH versus the crystallinity of the original fluoropolymer matrix. Open symbols indicate samples preequilibrated in liquid water. Closed symbols indicate samples preequilibrated at lower relative humidities.

State of water

The melting and crystallization of water absorbed by the membranes from liquid-phase water was followed by DSC. Typical melting thermograms are shown in

Figure 3. Both the radiation-grafted membranes and the Nafion materials present a broad peak around 0°C attributable to free freezing water. A second, smaller peak, attributed to freezing bound water, is seen at

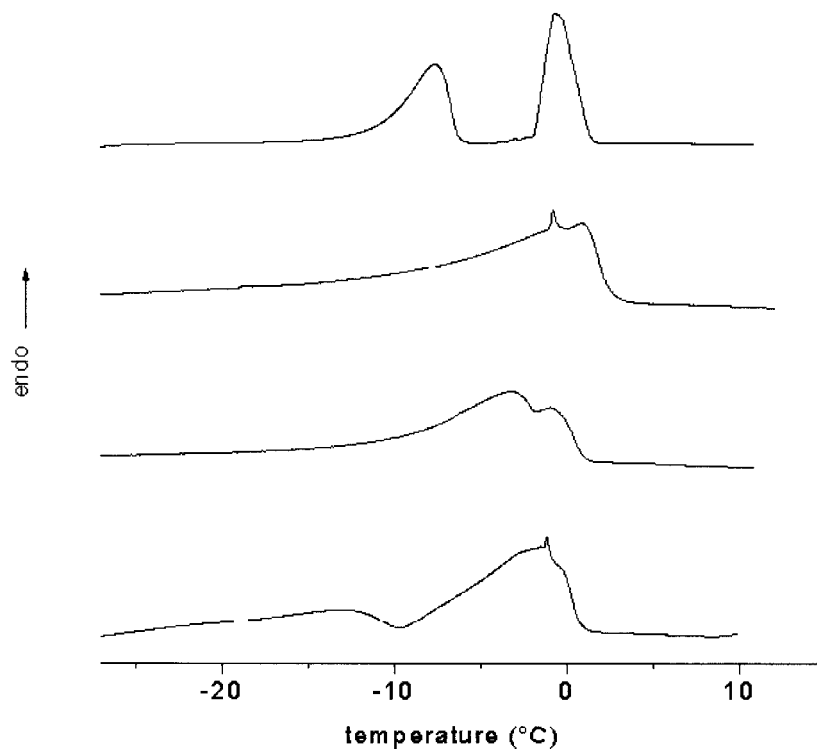


Figure 3 DSC melting thermograms of water in the membranes. From top to bottom: porous silica (nominal diameter 8.2 nm), Nafion 117, FEP-g-PSSA, and (PVDF-co-HFP 6%)-g-PSSA.

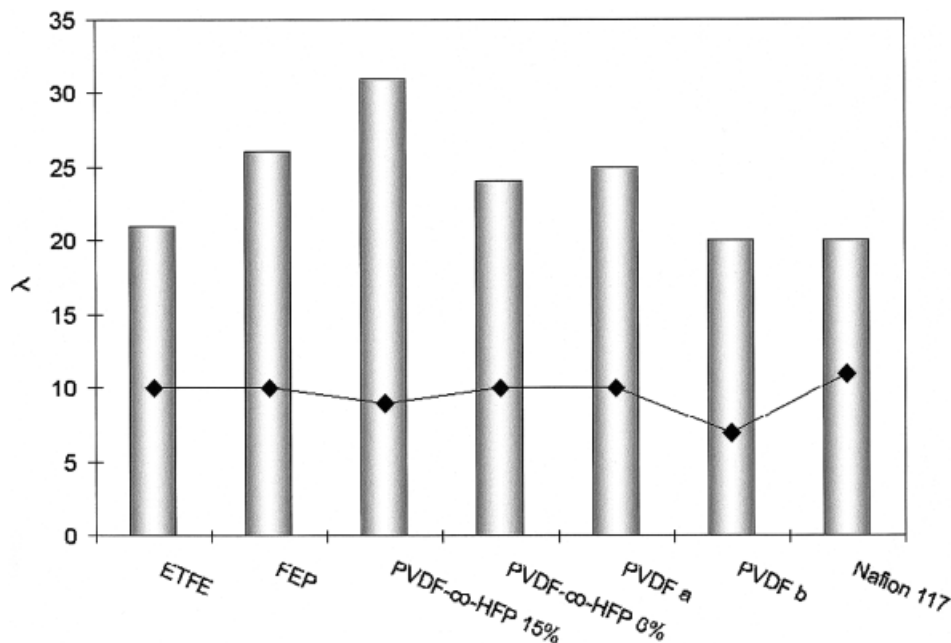


Figure 4 Total water uptake (columns) and nonfreezing water uptake (line) of the DSC samples.

temperatures ranging from, roughly, -15 to -1°C , depending on the membrane.

The area under the peaks was integrated, and with the melting enthalpy of water, the corresponding amount of freezing water absorbed was calculated. After the DSC measurements, the water uptake was determined gravimetrically and compared with the water uptake calculated from the DSC data. The difference was attributed to nonfreezing water tightly bound to the sulfonic acid groups in the first hydration shell.^{12,19} The water uptakes are plotted in Figure 4. The amount of nonfreezing water here is the same for all samples and corresponds to around 10 water molecules per sulfonic acid group (line in Fig. 4). This value is higher than the 6 molecules reported by Randin for Nafion and various others sulfonic acid containing polymers,¹⁵ and Gupta et al. found 6 to 8 molecules of nonfreezing water in poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP)-*g*-PSSA.¹⁹ However, our value may have been overestimated: experimental error in DSC measurements is large as the integration limits can be difficult to define. Previous work in our group found a similar amount of nonfreezing water in crosslinked, radiation-grafted PVDF-*g*-PSSA membranes where graft penetration had occurred¹³ and in sulfonated, proton-irradiated poly(vinyl fluoride) (PVF).²⁰ The number of molecules of nonfreezing water was consistent with the λ reached in the first part of the sorption curve, and both were independent of the structure of the sulfonated membrane.

The melting thermograms of water in Figure 3 show that in some cases, the distinction between the two

peaks corresponding to free freezing water and freezing bound water was clear, but for the FEP and PVDF-co-HFP 15% based materials, the curve resembled rather a bimodal peak. These two samples also had the highest water uptake from the liquid phase and the highest conductivity at 100% RH. The depression of the melting point of water has been correlated with the pore diameter in various well-defined systems such as porous silica,²¹ and a similar analysis has been applied to Nafion 117 samples.²² As an indication of the similarities and differences, Figure 3 also shows the melting of water in porous silica of nominal pore diameter 8.2 nm. If the relationship between pore size and depression of the melting point determined by Cappadonia et al. for Nafion 117²² is used here, the pore size in the radiation-grafted membranes varied from 2 to 4 nm, with membranes with higher water uptakes having larger pores. This suggests that the larger, macroscopic swelling of the more amorphous radiation-grafted materials was a reflection of an increase in the pore size in these membranes on hydration.

The crystallization data for water contained in these membranes revealed a difference between the Nafion and the PSSA-containing membranes (Fig. 5). The Nafion materials presented a broad crystallization peak, whereas for the radiation-grafted materials, the peak was narrow. The temperature of crystallization varied between -20 and -25°C (a drop of water crystallized at -19°C). The difference in the shape of the peak seemed to indicate differences in the water bonding, attributable maybe to the existence of a range of environments in the

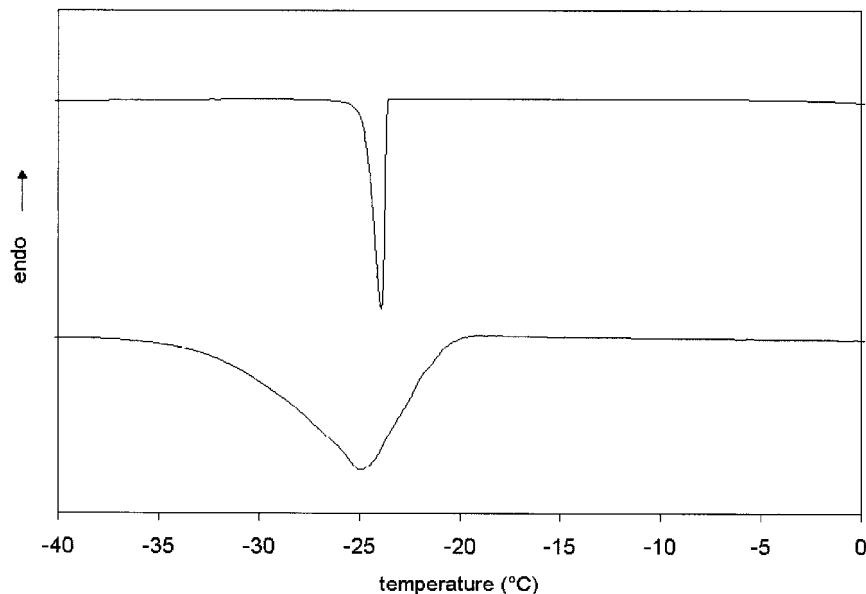


Figure 5 DSC crystallization thermograms of water in the membranes. From top to bottom: FEP-g-PSSA and Nafion 105.

Nafion materials absent from the radiation-grafted materials, where the water appeared to be in a more homogeneous environment.

NMR measurements

NMR measurements showed differences in the T_1 values. The T_1 relaxation time of the spins of a liquid confined in a porous solid matrix gives a measure of the liquid–solid interactions. The higher the extent of interaction is, the faster the spins relax and the smaller the relaxation time is. This relates directly to the surface area in the solid and, in the case of a porous system, to the pore size inside the matrix. As

seen in Figure 6, the T_1 values of the Nafion 117 sample were significantly higher at all water contents than the values of any of the grafted membranes. This could be explained by more solid–liquid interactions in the radiation-grafted materials and a less homogeneous, more clustered structure in the Nafion materials, where in addition to the solid–liquid interactions, there are significant liquid–liquid interactions. The increase in T_1 with λ in Nafion then would then point to an increase in the cluster size and a greater proportion of water–water interactions. Such a difference in structure with the radiation-grafted materials would be consistent with the DSC crystallization data, the variation in the

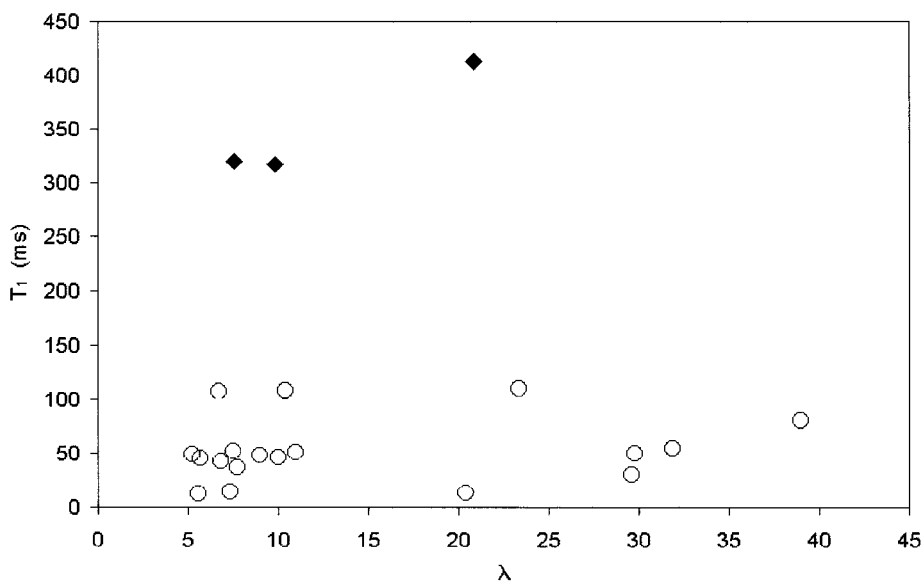


Figure 6 T_1 's in (◆) Nafion 117 and (○) radiation-grafted membranes.

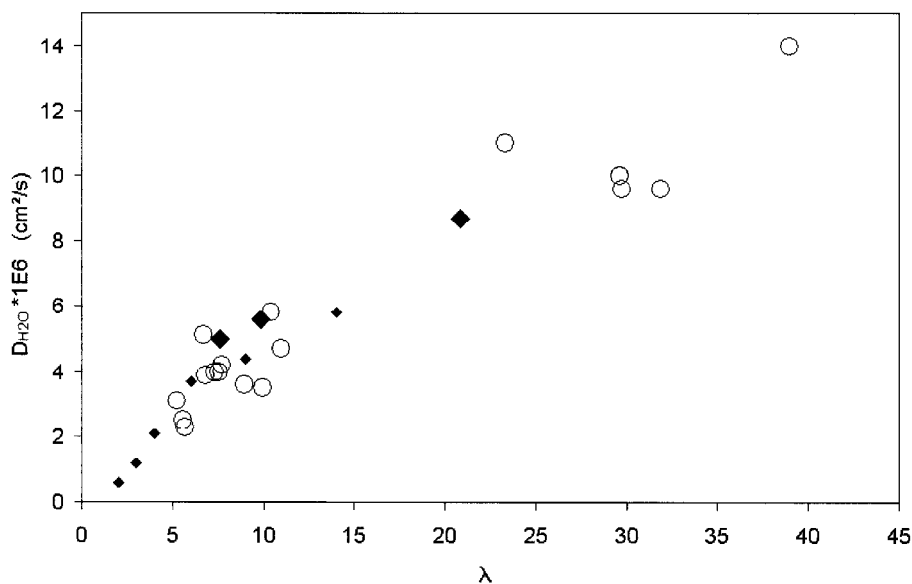


Figure 7 Water $D_{\text{H}_2\text{O}}$ of (○) radiation-grafted membranes and Nafion 117: (◆) this work and (◇) ref. 16.

surroundings of the water molecules in Nafion leading to a broader peak. The T_1 values of the grafted membranes were broadly similar, indicating that the fluoropolymer matrix played only an indirect part in the water management.

Zawodzinski et al. used PFG NMR diffusion measurements to determine the diffusion coefficients of water and protons in Nafion,¹⁶ and our group previously applied the same technique to PVDF-*g*-PSSA membranes.²³ Figure 7 shows the $D_{\text{H}_2\text{O}}$ of the various samples versus the water content in terms of molecules of water per sulfonic acid group. At similar water contents, the results for Nafion 117 were fairly close to those obtained by Zawodzinski et al. (also shown). At first sight, all the membranes appeared to behave very similarly. The $D_{\text{H}_2\text{O}}$ of the radiation-grafted samples displayed the same dependence on water content. In contrast, our earlier investigation found distinct dependencies for PVDF-*g*-PSSA membranes of different degrees of grafting,²³ with samples of lower degrees of grafting having noticeably smaller water $D_{\text{H}_2\text{O}}$. This would indicate that the IEC and the corresponding total water uptake influenced the water $D_{\text{H}_2\text{O}}$. If this is the case, Nafion 117 was in fact behaving quite differently from the other materials: its IEC

was about half that of the radiation-grafted membranes, and the total amount of water present was significantly lower. The $D_{\text{H}_2\text{O}}$ of water seems, therefore, to be in part determined by the morphology of the material. Once again, the lack of direct influence of the nature of the fluoropolymer in radiation-grafted membranes was apparent.

Conductivity measurements

The conductivities of all the membranes were of the same order and were between 40 and 110 mS/cm in the fully hydrated state (cf. Table II). When the RH decreased, the conductivity data for the Nafion and radiation-grafted materials differed at intermediate water contents. At 84% RH, the water uptake was around six to seven molecules of water per sulfonic acid group for all samples. However, whereas the conductivity of the radiation-grafted materials dropped to around 5 mS/cm, that of the perfluorinated materials was four times higher. Although the conditions did not fulfill all the requirements, applying the Nernst-Einstein equation for strong electrolytes could give us an estimation of the proton diffusion coefficient.^{16,23} In Figure 8, the proton diffusion coefficient and the water

TABLE II
Conductivities (mS/cm) at Room Temperature of Some Membranes at Various Relative Humidities

| | Degree of grafting (%) | 100% RH | 92% RH | 84% RH | 33% RH | Dried over P ₂ O ₅ |
|---|------------------------|---------|--------|--------|--------|--|
| PVDF a- <i>g</i> -PSSA | 36 | 66 | 29 | 4.6 | 0.4 | Not detectable |
| PVDF- <i>co</i> -HFP 15% <i>g</i> -PSSA | 40 | 110 | 44 | 3.3 | 0.003 | Not detectable |
| FEP- <i>g</i> -PSSA | 34 | 108 | 25 | 5.1 | 0.1 | Not detectable |
| Nafion 117 | — | 51 | 36 | 20 | 1.6 | Not detectable |
| Nafion 105 | — | 56 | 44 | 24 | 0.7 | Not detectable |

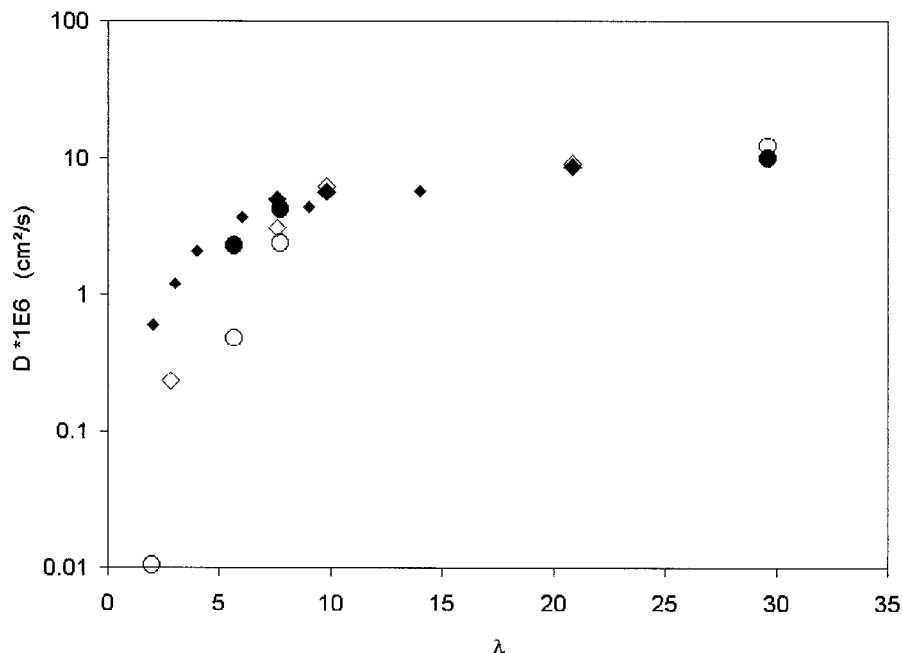


Figure 8 D_{H_2O} of Nafion 117 from (◆) this work and (♦) ref. 16 and of (●) FEP-g-PSSA and the proton diffusion coefficient of (◇) Nafion 117 and (○) FEP-g-PSSA.

diffusion coefficient of Nafion 117 and a radiation-grafted membrane (FEP-g-PSSA) have been plotted versus λ . The data show that at high water contents, the proton diffusion coefficient in radiation-grafted membranes were similar to those of the Nafion materials, and for all membranes they were similar to the water diffusion coefficient. At intermediate water contents, a gap appeared between the proton and water diffusion coefficient in the radiation-grafted membranes but not in the Nafion materials. This confirms findings reported earlier.²³ The high proton diffusion coefficient in Nafion were attributed to a particular ability of the material to reorganize and create channels for proton conduction.²⁴ In radiation-grafted membranes, acid groups are not able to rearrange as freely into clusters, and thus, the sulfonic acid groups are more evenly distributed. Because of this restricted mobility, some acid groups might be isolated from the conductivity paths at intermediate water contents, decreasing the passages of proton through the membrane. In addition, PSSA is a weaker acid than Nafion, which, together with the more dispersed acid group distribution, results in stronger interactions between protons and sulfonic acid groups.²⁴ Both these phenomena restrict the proton transport through the membrane resulting in a lower proton D_{H_2O} in the experimental membranes.

CONCLUSIONS

The water in radiation-grafted membranes and the water in Nafion membranes present some similarities:

the general sorption pattern is the same. Furthermore, DSC measurements show that the amount of non-freezing water tightly bound to the sulfonic acid groups is identical for all membranes. Differences between radiation-grafted membranes appear at very high relative humidities when the membrane has first been immersed in boiling water: the crystallinity of the membrane and, therefore, of the starting material then influences the water uptake, and DSC thermograms suggest differences in the pore size, with higher water uptakes being accompanied by larger pores and higher conductivities. In contrast, when sorption takes place from the vapor phase alone, the fluoropolymer matrix appears to have no influence on the water uptake. In general, although the starting material acts as a host for the PSSA grafts, there appears to be very little interaction between the fluoropolymer and hydrophilic parts of the membrane.

The behavior of the radiation-grafted membranes differs from that of the Nafion membranes at intermediate hydration levels. Although the water uptakes are similar, the conductivity of Nafion is higher. This reflects lower proton D_{H_2O} 's in the radiation-grafted materials at these water uptakes. The difference in behavior is attributable to a different structure in Nafion, which favors proton transport. Structural factors are also suggested by the lower T_1 values in radiation-grafted membranes.

References

1. Lehtinen, T.; Sundholm, G.; Holmberg, S.; Sundholm, F.; Björnbom, P.; Bursell, M. *Electrochim Acta* 1998, 43, 1881.

2. Brack, H. P.; Büchi, F. N.; Huslage, J.; Scherer, G. G. Proc 194th Electrochem Soc Meeting 1998, 98-27, 52.
3. Munari, S.; Vigo, F.; Tealdo, G.; Rossi, C. J. *J Appl Polym Sci* 1967, 11, 1563.
4. Nasef, M.; Saidi, H.; Nor, H. M.; Dahlan, K. M.; Hashim, K. J. *J Appl Polym Sci* 1999, 73, 2095.
5. Walsby, N.; Sundholm, F.; Kallio, T.; Sundholm, G. *J Polym Sci Part A: Polym Chem* 2001, 39, 3008.
6. Davis, T. A.; Genders, J. D.; Pletcher, D. In *A First Course in Ion-Exchange Membranes*; Electrochemical Consultancy: Romsey, UK, 1997; Chapter 3.
7. Hietala, S.; Skou, E.; Sundholm, F. *Polymer* 1999, 40, 5567.
8. Wexler, A. In *CRC Handbook of Chemistry and Physics*, 73rd ed.; Lide, D. R., Ed.; 1992; p 15.
9. Mauritz, K. A. In *Ionomers: Synthesis, Structure, Properties and Applications*; Tamt, M. R.; Mauritz, K. A.; Wilkes, G. L., Eds.; Blackie Academic and Professional: London, 1997; Chapter 3.
10. Hsu, W. Y.; Gierke, T. D. *J Membr Sci* 1983, 13, 307.
11. Hietala, S.; Holmberg, S.; Karjalainen, M.; Näsman, J.; Paronen, M.; Serimaa, R.; Sundholm, F.; Vahvaselkä, S. *J Mater Chem* 1997, 7, 721.
12. Hietala, S.; Holmberg, S.; Näsman, J.; Ostrovskii, D.; Paronen, M.; Serimaa, R.; Sundholm, F.; Torell, L.; Torkkeli, M. *Angew Makromol Chem* 1997, 253, 151.
13. Elomaa, M.; Hietala, S.; Paronen, M.; Walsby, N.; Jokela, K.; Serimaa, R.; Torkkeli, M.; Lehtinen, T.; Sundholm, G.; Sundholm, F. *J Mater Chem* 2000, 10, 2678.
14. Gierke, T. D.; Munn, G. E.; Wilson, F. C. *J Polym Sci Polym Phys Ed* 1981, 19, 1687.
15. Randin, J.-P. *J Electrochem Soc* 1982, 129, 1215.
16. Zawodzinski, T. A.; Neeman, M.; Sillerud, L. O.; Gottesfeld, S. *J Phys Chem* 1991, 95, 6040.
17. Gottesfeld, S.; Zawodzinski, T. A. *Adv Electrochem Sci Eng* 1997, 5, 195.
18. Zawodzinski, T. A.; Derouin, C.; Radzinski, S.; Sherman, R. J.; Smith, V. T.; Springer, T. E.; Gottesfeld, S. *J Electrochem Soc* 1993, 140, 1041.
19. Gupta, B.; Haas, O.; Scherer, G. G. *J Appl Polym Sci* 1995, 57, 855.
20. Paronen, M.; Karjalainen, M.; Jokela, K.; Torkkeli, M.; Serimaa, R.; Juhanoja, J.; Ostrovskii, D.; Sundholm, F.; Lehtinen, T.; Sundholm, G.; Torell, L. *J Appl Polym Sci* 1999, 73, 1273.
21. Rennie, G. K.; Clifford, J. *J Chem Soc Faraday Trans* 1977, 73, 680.
22. Cappadonia, M.; Erning, J. W.; Saberi Niaki, S. M.; Stimming, U. *Solid State Ionics* 1995, 77, 65.
23. Hietala, S.; Maunu, S. L.; Sundholm, F.; Lehtinen, T.; Sundholm, G. *J Polym Sci Part B: Polym Phys* 1999, 37, 2893.
24. Kreuer, K. D.; Dippel, T.; Maier, J. *Proc Electrochem Soc* 1995, 95-23, 241.